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A theoretical study of the H_3O^+ ion

By Ragnar Grahn

With 1 figure in the text

ABSTRACT

A survey of experimentally known facts is given. The electronic structure of the H_3O^+ ion has been studied by the LCAO MO method. Three different values of the H–O–H angle have been considered and the question of the equilibrium angle, which is not known experimentally, is discussed. The results give a slight preference to a value of the H–O–H angle just in the neighbourhood of 120°, i.e. a very flat molecule ion. The proton affinity of the water molecule is obtained in satisfactory agreement with the experimental value. Population analysis and transformation to two different sets of equivalent orbitals have been made.

I. Introduction

Very few experimental data are known about the structure of the hydronium ion H_3O^+. Most of these have been obtained by investigation of the properties of crystals which contain H_3O^+ ions embedded in the crystal lattice.

The ion itself has, however, for a long time been expected to be a stable entity for thermodynamical reasons [1]. By studing the rapid proton transfer in water it has been found that the lifetime of the H_3O^+ complex is probably about 10^{-13} sec [2, 3] before leaving a proton for an adjacent H_2O molecule.

This time is greater than the characteristic time of the molecular vibrations by about a factor of 10.

Some difficulties in the explanation of the abnormal proton mobility and the UV absorption in acidic solutions can be accounted for, according to Wicke, Eigen and Ackermann [3, 4], by supposing H_3O^+ ions to be surrounded by a hydration shell, thus forming a stable pyramidal $H_9O_4^+$ complex.

In 1957 Falk and Giguère [5] gave more direct experimental evidence for the existence of the ion in solutions of strong acids. They detected it with infrared spectroscopy. Their data support the idea that it exists long enough to undergo normal vibrations.

In the experimental studies discussed below data were not obtained for free ions but for ions in some way linked to other molecules. The binding forces, of course, also affect the structure of the H_3O^+ to some extent. This influence will be discussed later in the paper. It is, however, very interesting for our purposes to study the experimental data because they give a good idea of the limits within which the molecular parameters may vary.

IR and Raman spectra

Bethell and Sheppard [6] identified the vibration spectrum of $H_3O^+NO_3^-$ and $H_3O^+ClO_4^-$. Ferriso and Hornig [7] found, in a study of the ionic crystals OH_3F, OH_3Cl, OH_3Br, OH_3I and OD_3Cl the four fundamental frequencies expected for a symmetrical pyramid. For their analysis they assumed tetrahedral angles and an O–H distance of 0.98 Å.

The same O–H distance was used in an analysis of the vibration spectrum of the hydronium ion in hydronium perchlorate, obtained by Taylor and Vidale [8] using three different H–O–H angles, 107°, 111° and 115°. They found that there might perhaps be a slight perference for 107°.

NMR spectra

With the aid of NMR spectra of some acid monohydrates below −130°C, Richards and Smith [9] were able to identify the H_3O^+ ion and calculate the O–H distance to 1.02 Å, the H–H distance to 1.72 Å and the angle H–O–H to 115°. There is good agreement between the results obtained by them for different monohydrates.

The results of similar studies of the NMR spectrum of hydrogen perchlorate monohydrate performed by Kakiuchi *et al.* [10] gave the results 0.98 Å, 1.58 Å and 110°.

X-ray spectra

In 1924 an X-ray study of $HClO_4$–H_2O was made by Volmer [11]. By comparison with the corresponding X-ray data of ammonium perchlorate he found that the configuration of the atoms in the two associations were similar, which indicates a symmetric top configuration for H_3O^+ like that of NH_3. In later years direct observation of the diffraction pattern of the hydrogen atoms in crystals have been possible. The effect is very weak, however, and the positions of the H atoms can only be determined with a standard deviation of about 0.07 Å. Luzzati [12, 13] investigated the diffraction pattern in crystalline $HNO_3 \cdot 3H_2O$. He obtained different individual values for the three O–H distances, depending on their positions in the crystal lattice: 1.00, 0.85, and 1.10 Å. The angles between the O–H···O hydrogen bonds in which the hydrogen atoms take part are 113°, 118°, and 103°. The average distance from the hydrogen atoms to the O–O line is found to be 0.12 Å.

Young Ku Yoon and Carpenter [14] determined the crystal structure of hydrogen chloride monohydrate by X-ray diffraction. They obtained the value 0.96 ± 0.08 Å for the O–H distance and approximately 117° for the H–O–H angle. The distance between a hydrogen atom and the line joining the oxygen atom to the corresponding chlorine atom was found to be 0.10 Å, which is almost the same as in the investigations by Luzzati.

Theoretical studies

In 1925 Hund [15] made an attempt to determine the structure of the hydronium ion by theoretical methods. He estimated with the aid of spectra of certain molecules the potential of some atomic ions, which made it possible to calculate the probable configuration of H_2O and H_3O^+ among others. He found for H_2O the values 1.03 and 1.09 Å for the O–H and H–H distances respec-

Table 1. Experimental and theoretical investigations of H_3O^+. Distances in Ångström units.

Authors	Molecules invest.	H–H dist.	H–O dist.	H–O–H angle	Angle between H bonds	Method
Bethell & Sheppard 1953	$H_3O^+NO_3^-$ $H_3O^+ClO_4^-$					IR
Ferriso & Hornig 1955	Hydrogen halides		0.98	Tetrahedral		IR
Taylor & Vidale 1956	$H_3O^+ClO_4^-$		0.98	107°		IR
Richards & Smith 1951	$H_3O^+NO_3^-$ $H_3O^+ClO_4^-$ $H_3O^+HSO_4^-$	1.72 ± 0.02	1.02	115°		NMR
Kakiuchi *et al.* 1951	$H_3O^+ClO_4^-$	1.58	0.98	110°		NMR
Volmer 1924	$H_3O^+ClO_4^-$					X-ray
Luzzati 1953	$HNO_3 \cdot 3H_2O$		1.00, 0.85, 1.10		113°, 118°, 103°	X-ray
Young Ku Yoon & Carpenter 1959	$HCl \cdot H_2O$	1.65	0.96	117°	110.4°	X-ray
Hund 1925		1.11	1.05			Theor.

tively. Corresponding values for H_3O^+ were 1.05 and 1.11 Å, which means much more peaked forms for the molecules than they have later been believed to have. Another result of his calculations was the value 180 (± 40) kcal/mole for the proton affinity of water, which is in excellent agreement with values found later (see part V). This agreement possibly has its root in the semi-empirical nature of his investigation, where known experimental data are used at the beginning of the calculations. Table 1 gives an abstract of the results discussed above.

The aim of the present work is to obtain a molecular orbital (MO) description of the H_3O^+ ion when unaffected by charges of neighbouring atoms and ions. As is seen from the preceding, there are no definite values of angles and interatomic distances given as a starting point for such a calculation. The only experimental values of these parameters have been obtained from H_3O^+ ions in ionic crystals. These data must therefore deviate from those for a free ion and also must vary among themselves because they are taken from crystals of different complexes. In addition to this there are rather great uncertainties in the determination of the atomic positions of a given crystal, especially the positions of hydrogen atoms. For example, the standard deviation of determinations of hydrogen positions with the X-ray method is about 0.07 Å. However, from the results given in Table 1 it can be seen that the H–O–H angle preferably occurs in the interval 100°–120°. A tendency towards a more precise value is difficult to find. For a better understanding of the behaviour of the ion in its different associations we have chosen to study it assuming three different H–O–H angles: 100°, 110°, and 120°. For a free H_3O^+ ion it would, however, be justified to assume the equilibrium angle not smaller than in water, about 105°.

Concerning the O–H distance, a study of Table 1 makes it seem convenient to choose a value in accordance with the statement by Richards and Smith [9]:

"By comparison with ammonia and the ammonia ion we might expect the increase in OH bond length, in passing from water to H_3O^+, to be about 0.01 Å ... ." There is probably no real disadvantage in putting the O–H distance equal to that in the water molecule. This would simplify our computations a great deal, because we could then use the electron integrals used by Ellison and Shull [16, 17] in their study of the water molecule. Therefore we have chosen to make the study using the O–H distance of water 0.9581 Å, and the angles 100°, 110°, and 120.

II. Wave functions

The system consists of one oxygen nucleus, O, three hydrogen nuclei H_1, H_2, and H_3, supposed to be arranged symmetrically, and ten electrons, whose configuration is to be determined (see Fig. 1). The symmetry group is C_{3v} and for the flat molecule (H–O–H angle 120°) D_{3h}. In the ground state the electron configuration is to be described by five doubly occupied molecular orbitals (MO's) ϕ_i. The total wave function is formed with the aid of a Slater determinant:

$$\Psi = N \begin{vmatrix} \alpha(1)\phi_1(1) & \alpha(2)\phi_1(2) & \alpha(3)\phi_1(3)\ \ldots \\ \beta(1)\phi_1(1) & \beta(2)\phi_1(2) & \beta(3)\phi_1(3)\ \ldots \\ \alpha(1)\phi_2(1) & \alpha(2)\phi_2(2) & \alpha(3)\phi_2(3)\ \ldots \\ \vdots & \vdots & \vdots \end{vmatrix} \tag{1}$$

where 1, 2, 3 ... denote the coordinates of the electrons. α and β are functions representing the two possible spin orientations. Each MO is formed as a linear combination of atomic orbitals (LCAO):

$$\phi_i = \sum_{k=1}^{n} a_{ik}\chi_k \tag{2}$$

where χ_k are atomic orbitals (AO's) centered on the different atoms in the molecule. The atomic orbitals (see Fig. 1) used here are:

Oxygen: $1s$, $2s$, $2px$, $2py$ $2pz$, abbreviated o, s, x, y, z,
Hydrogen: $1s$ on each hydrogen atom denoted by h_1, h_2, h_3.

The $2s$ function has been made orthogonal to $1s$ by giving it a node according to $2s = (1-S^2)^{-\frac{1}{2}}(2s' - S\cdot 1s)$, where $2s'$ is nodeless. S is the overlap of $1s$ with $2s'$. Orbital exponents are given by Slater's rules: oxygen $1s$ 7.7, $2s'$, $2px$, $2py$, $2pz$ 2.275, hydrogen $1s$ 1.0. The best coefficients a_{ik} can be determined by minimizing the energy

$$E = \int \Psi^* H \Psi \, d\tau \tag{3}$$

of the system described by Ψ. The hamiltonian H has the following form:

$$H = -\sum_{i=1}^{10}\left(\frac{\hbar^2}{2m}\Delta_i + \frac{8}{r_{Oi}} + \sum_{k=1}^{3}\frac{1}{r_{H_k i}}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}. \tag{4}$$

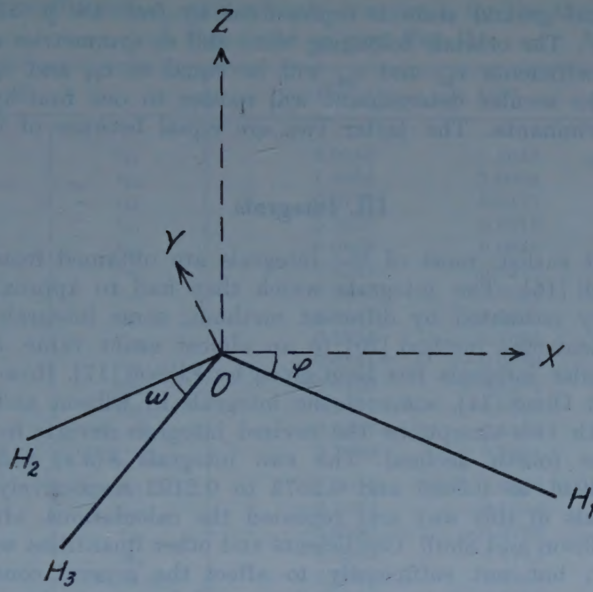

Fig. 1. The coordinate system describing the atomic orbitals. The z axis is directed along the molecular axis. The xy plane is parallel to the $H_1H_2H_3$ plane. O and H_1 are in the xz plane.

The problem is further treated according to the iteration method developed by Roothaan [18]. To facilitate the solution of the secular equation which arises from the minimum condition it is better to express the MO's as linear combinations of symmetry orbitals (SO's) which are combinations of the AO's earlier mentioned. The SO's which form a basis for the irreducible representations of the symmetry group, can be obtained with the aid of Wigner's projection operators [19]. The transformation to the SO's σ_i can be written:

$$a_1 \begin{cases} \sigma_1 = \dfrac{1}{\sqrt{3}}(h_1 + h_2 + h_3) \\ \sigma_2 = o \\ \sigma_3 = s \\ \sigma_4 = -z, \end{cases} \qquad \begin{matrix} e_- \begin{cases} \sigma_5 = \dfrac{1}{\sqrt{2}}(h_2 - h_3) \\ \sigma_6 = y, \end{cases} \\ e_+ \begin{cases} \sigma_7 = \dfrac{1}{\sqrt{6}}(2h_1 - h_2 - h_3) \\ \sigma_8 = x, \end{cases} \end{matrix} \tag{5}$$

where the symmetry types are written before each group.

The MO's are now obtained as linear combinations of the symmetry orbitals:

$$\begin{aligned} \phi_i &= (n a_1) = \sum_{k=1}^{4} c_{ik} \sigma_k \quad \text{for } i = 1 \ldots 4 \\ \phi_i &= (n e_-) = c_{i5}\sigma_5 + c_{i6}\sigma_6 \quad \text{for } i = 5, 6 \\ \phi_i &= (n e_+) = c_{i7}\sigma_7 + c_{i8}\sigma_8 \quad \text{for } i = 7, 8. \end{aligned} \tag{6}$$

The symmetrical ground state is represented by (ref. 18, p. 83): $(1a_1)^2(2a_1)^2(3a_1)^2(1e_-)^2(1e_+)^2$. The orbitals belonging to e_- and e_+ symmetries are degenerate. Therefore the coefficients c_{55} and c_{56} will be equal to c_{77} and c_{78} respectively.

In this way the secular determinant will reduce to one four-by-four and two two-by-two determinants. The latter two are equal because of the degeneracy mentioned above.

III. Integrals

As pointed out earlier, most of the integrals are obtained from the tables by Ellison and Shull [16]. The integrals which they had to approximate in some way, they usually estimated by different methods; some integrals were also expanded by Ruedenberg's method [20] to an almost exact value. A separate discussion of molecular integrals has been given by Ellison [17]. However, according to McWeeny and Ohno [34], some of the integrals in Ellison and Shull's paper are in error. With two exceptions the revised integrals deviate from the original ones only in the fourth decimal. The two integrals $S(h's)$ and $(h'z' : ss)$ are revised from 0.4946 to 0.5086 and 0.2073 to 0.2193 respectively. We changed these two integrals in this way and repeated the calculations, after first having used those of Ellison and Shull. Coefficients and other quantities where somewhat changed thereby, but not sufficiently to affect the general conclusions drawn from them. The remaining integrals of three- and four-center type we have tried to compute with accuracy to the third decimal. This is described in more detail in the appendix.

IV. Final coefficients and orbital energies

The final coefficients making the iteration procedure self-consistent are listed in Table 2, together with one-electron energies in atomic units.

As might be expected, the mixing between the oxygen $1s$ orbital σ_2 and the others is small. However, it is not negligible. In their calculation on the water molecule Ellison and Shull [16] made, besides a complete calculation allowing such mixing, one other more approximate calculation where they did not allow mixing, letting the $1s$ electrons belong to the oxygen core. The results of these calculations differed by about 20 % both in dissociation energy and dipole moment. Discrepancies caused by neglect of $1s$ mixing in this case seem to be of about the same magnitude as the discrepancies in results obtained by conventional LCAO MO calculations, which are caused by the approximate nature of this method.

The values of ε_i, which give good approximations to the negatives of the corresponding ionization energies, show a definite difference between occupied and unoccupied orbitals in the entire investigated angle interval. The effect of configurational interaction would therefore be supposed small.

V. Total energy and proton affinity of water

The total energy for the different angles appears in Table 3. The expression giving the energy as a function of the angle φ (see Fig. 1) must be even in φ by symmetry arguments. The lowest polynomial fitting our computed values is

Table 2. Final coefficients c_{ik} and orbitals energies ε_i for the three different values of the angle ω (see Fig. 1).

ω		100°	110°	120°
Occupied	c_{11}	-0.0046	-0.0045	-0.0044
	c_{12}	1.0004	1.0004	1.0004
	c_{13}	0.0178	0.0177	0.0176
	c_{14}	0.0027	0.0019	0
	c_{21}	0.0953	0.0848	0.0780
	c_{22}	-0.0233	-0.0223	-0.0217
	c_{23}	0.8867	0.9096	0.9286
	c_{24}	0.1947	0.1400	0
	c_{31}	0.2372	0.1694	0
	c_{32}	-0.0221	-0.0159	0
	c_{33}	-0.4460	-0.3169	0
	c_{34}	0.8777	0.9397	1
	$c_{55}=c_{77}$	0.5397	0.5419	0.5495
	$c_{56}=c_{78}$	0.7269	0.7081	0.6880
Unoccupied	c_{41}	1.0076	1.0458	1.0771
	c_{42}	-0.1013	-0.1054	-0.1087
	c_{43}	-0.9236	-0.9739	-1.0209
	c_{44}	-0.5264	-0.3748	0
	$c_{65}=c_{87}$	1.3683	1.3341	1.3091
	$c_{66}=c_{88}$	-0.8826	-0.9140	-0.9448
Occupied	ε_1	-21.0608	-21.0468	-21.0410
	ε_2	-1.8440	-1.8171	-1.7944
	ε_3	-0.9718	-0.9516	-0.9392
	$\varepsilon_5=\varepsilon_7$	-1.0986	-1.1156	-1.1356
Unoccupied	ε_4	0.0090	0.0651	0.1108
	$\varepsilon_6=\varepsilon_8$	0.1025	0.0947	0.0675

Table 3. Total molecular energy for H_3O^+ and proton affinity of water.

ω	100°	110°	120°	Exp.
Total energy in a.u.	-76.0836	-76.1407	-76.1820	-76.725
Proton affinity of water in kcal/mole	202	238	264	169 [27]

then of fourth degree. This function has one extremum in the interval: a minimum at $\varphi=0$, which means $\omega=120^\circ$. The experimental data mentioned in the introduction indicate the possibility of obtaining a minimum point just below 120° and a flat maximum at 120° (see discussion, part I).

The value of the proton affinity, which is the heat evolved in the reaction $H_2O+H^+\rightarrow H_3O^+$, is given as the difference between the total energy of the water molecule and the H_3O^+ ion. For a theoretical calculation the most consistent way to choose the water energy is in this case to take the value calculated by the same method and with the same basic orbitals as for H_3O^+. The energy at the experimental equilibrium angle is according to McWeeny and Ohno [34] -2061.0 e.v. $=-75.761$ a.u. The difference between this and the total energies of H_3O^+ are 202, 238, and 264 kcal/mole, for the angles 100°, 110°, and 120° respectively (Table 3).

The experimental value appears to lie between 150 and 200 kcal/mole. Sherman [24] calculated it with the thermochemical equation

$$P_{H_2O} = P_{NH_3} + Q_{NH_3} - Q_{H_2O} + Q_{H_3OClO_4} - Q_{NH_4ClO_4}$$

and obtained the result 182 kcal/mole. The value of Sherman corrected to 188 kcal/mole [25] has been the value generally accepted. Later on Vetchinkin, Pshenichnov, and Sokolov [26] pointed out that if a correction is made accounting for the energies of the hydrogen bonds related to the hydrogen atoms in H_3O^+ instead of making rougher models of the ion in the calculations of some lattice energies, the energy will be lowered to about 170 kcal/mole. This is in very good agreement with the value obtained by Tal'rose and Frankevich [27]—169 ± 2 kcal/mole—with the mass spectroscopic method (see also ref. 28).

The affinity obtained from our theoretical investigation may be said to be satisfactory, especially since the total affinity is only 0.55 % of each of the two quantities whose difference it is.

VI. Equivalent orbitals

The MO's in (6) have been transformed to equivalent orbitals (EO's) [29]. In this case the EO's will consist of three equivalent bonding orbitals χ_{b1}, χ_{b2}, and χ_{b3}, one lone-pair electron orbital χ_l and one oxygen inner shell orbital. The last is supposed to constitute the molecular orbital ϕ_1. The four remaining MO's ϕ_2, ϕ_3, ϕ_5, and ϕ_7 then undergo a unitary transformation to the four equivalent orbitals $\chi_{b1} \dots \chi_{b3}$ and χ_l. This transformation is not uniquely determined by the requirement that the χ's are orthogonal and equivalent. We can put one more condition upon them. The equivalent orbitals for two different forms of this condition have been evaluated:

(i) The lone-pair electron orbitals χ_l shall contain only oxygen atomic orbitals.
(ii) The oxygen hybrid part of the bonding orbitals shall be directed along the O–H direction.

As can be seen from Table 4, the two conditions do not differ very much from one another. In case (i) the bonding hybrid is put further away from the lone-pair hybrid than in case (ii). This inward bending of the bonds seems natural in view of the repulsion from the lone pair. The contribution from the hydrogen orbitals not belonging to the bond, b_{h2}, is weakly outward-bending, but cannot affect the charge distribution much.

In case (ii) we have forced the O-H direction upon the oxygen part of the bonding orbitals. The coefficient b_s which in case (i), $\omega = 100°$ and 110°, was small and of little importance for the charge density, has in case (ii) values indicating strong *sp* hybridization. Even the lone-pair orbital is in this case strongly hybridized. If we want bonding and lone-pair orbitals to have the property of pointing as much as possible away from each other, then picture (ii) is the most satisfying. This property is even more pronounced because the negative contribution l_h causes the lone pairs to be still more removed from the O-H region. Such mixing in lone-pair orbitals can be of importance in keeping them away from regions "reserved" for bonding electrons.

Table 4. Equivalent orbitals of H_3O^+ for different values of the H–O–H angle.

(i) no hydrogen contribution to χ_l			χ_{b1} and χ_l	(ii) O part of χ_{b1} along O–H_1 line		
$\omega=100°$	$\omega=110°$	$\omega=120°$		$\omega=100°$	$\omega=110°$	$\omega=120°$
0.5935	0.5781	0.5617	b_x	0.5935	0.5781	0.5617
−0.5121	−0.5214	0	b_z	−0.3130	−0.1984	0
−0.0479	0.0715	0.5361	b_s	0.3585	0.4720	0.5361
−0.0169	−0.0140	−0.0125	b_o	−0.0176	−0.0146	−0.0125
0.4450	0.4244	0.3923	b_{h1}	0.4216	0.4013	0.3923
−0.0947	−0.1175	−0.1572	b_{h2}, b_{h3}	−0.1181	−0.1406	−0.1572
0.1467	0.2954	1	l_z	0.7172	0.8858	1
0.9891	0.9553	0	l_s	0.7743	0.5095	0
−0.0134	−0.0128	0	l_o	0.0104	0.0106	0
0	0	0	l_h	−0.1016	−0.0846	0

The coefficients b_x, b_z, etc. are the coefficients of the AO's x, z, etc. in the equivalent bonding orbital χ_{b1}. The two other bonding orbitals are obtained through rotation of χ_{b1} ±120°. The lone-pair orbital coefficient l_h is the coefficient of each of the AO's h_1, h_2, and h_3 in EO χ_l. The notations (i) and (ii) refer to the two cases discussed in the text.

VII. Population analysis

Population analysis has been performed according to the scheme of Mulliken [30]. The results can be seen in Table 5. The notations in our special case may, however, be given some extra explanation:

Partial gross population in MO ϕ_i and AO h_k: $N(i; h_k)$.

Partial gross population in MO ϕ_i and all hydrogen atoms: $N(i; 3\,H) = \sum_{k=1}^{3} N(i; h_k)$.

Total gross population on one hydrogen atom: $N(H) = \sum_i \frac{N(i; 3\,H)}{3}$, where the summation is to be performed over all occupied MO's.

Net charge of one H atom: $Q\ (H) = 1 - N(H)$.

Partial overlap populations between SO σ_r and all hydrogen AO's in MO ϕ_i:

$$n(i, 3\,H, r) = \begin{cases} 4\,c_{i1}\,c_{ir}\,S_{1r} & \text{for } i = 1, 2, 3 \\ 4\,c_{55}\,c_{56}\,S_{56} = 4\,c_{77}\,c_{78}\,S_{78} & \text{for } i = 5, 7. \end{cases}$$

Subtotal overlap population between SO σ_r and all hydrogen AO's:

$$n(3\,H, r) = \sum_i n(i, 3\,H, r).$$

Total overlap population between oxygen and all hydrogen atoms in MO ϕ_i:

$$n(i, 3\,H, O) = \sum_r n(i, 3\,H, r)$$

where the summation runs over the oxygen SO's.

Table 5. Population analysis in the MO's and SO's of (6). Notations: see above and ref. 30.

ω	100°	110°	120°
N (1; 3 H)	−0.0010	−0.0010	−0.0010
N (2; 3 H)	0.1915	0.1648	0.1472
N (3; 3 H)	0.1311	0.0653	0
N (5; 3 H) = N (7; 3 H)	0.6477	0.6879	0.7313
N (a_1; H)	0.1072	0.0764	0.0487
N (e; H)	0.4318	0.4586	0.4875
N (H)	0.5390	0.5350	0.5363
N (1; 2)	2.0005	2.0005	2.0005
N (2; 2)	0.0006	0.0006	0.0006
N (3; 2)	−0.0001	−0.0001	0
N (2)	2.0010	2.0011	2.0011
N (1; 3)	0.0005	0.0005	0.0005
N (2; 3)	1.7216	1.7908	1.8523
N (3; 3)	0.2114	0.1063	0
N (3)	1.9335	1.8975	1.8527
N (1; 4)	0.0000	0.0000	0
N (2; 4)	0.0863	0.0439	0
N (3; 4)	1.6576	1.8285	2
N (4)	1.7439	1.8723	2
N (5; 6) = N (7; 8)	1.3523	1.3121	1.2687
n (1, 3 H, 2)	−0.0019	−0.0019	−0.0018
n (2, 3 H, 2)	−0.0009	−0.0008	−0.0007
n (3, 3 H, 2)	−0.0022	−0.0011	0
n (3 H, 2)	−0.0051	−0.0038	−0.0026
n (1, 3 H, 3)	−0.0003	−0.0003	−0.0003
n (2, 3 H, 3)	0.2979	0.2718	0.2551
n (3, 3 H, 3)	−0.3727	−0.1892	0
n (3 H, 3)	−0.0751	0.0823	0.2548
n (1, 3 H, 4)	0.0000	0.0000	0
n (2, 3 H, 4)	0.0209	0.0093	0
n (3, 3 H, 4)	0.2340	0.1245	0
n (3 H, 4)	0.2549	0.1338	0
n (1, 3 H, O)	−0.0022	−0.0022	−0.0021
n (2, 3 H, O)	0.3179	0.2803	0.2544
n (3, 3 H, O)	−0.1409	−0.0658	0
n (3 H, O)	1.3575	1.4495	1.5408
n (a, 3 H, O)	0.1747	0.2123	0.2522
n (5, 3 H, 6) = n (7, 3 H, 8)	0.5914	0.6186	0.6443
Q (H)	0.4610	0.4650	0.4637

Total overlap population between oxygen and all hydrogen atoms:

$$n(3\,\mathrm{H},\,\mathrm{O}) = \sum_i n(i,\,3\,\mathrm{H},\,\mathrm{O}).$$

As might be expected the net charge $Q(\mathrm{H})$ of the hydrogen atoms is strongly positive, about +0.46 for all the angles considered. The molecular orbitals of a_1 symmetry, ϕ_1, ϕ_2, and ϕ_3 have small contributions from the hydrogens. The total hydrogen population from them, $N(a_1,\,3\,\mathrm{H}) = \sum_{i=1}^{3} N(i,\,3\,\mathrm{H})$, varies between 0.15 and about 0.32, while that from the e orbitals ϕ_5 and ϕ_7 lies between 1.29 and 1.46.

The strong oxygen-hydrogen mixing in the e orbitals also make them the strongest bonding orbitals. The total overlap population between oxygen and all hydrogen atoms in each of the MO's ϕ_5 and ϕ_7, $n(5, 3\,\mathrm{H}, 6)$, is twice the corresponding population, $n(2, 3\,\mathrm{H}, \mathrm{O})$, in the bonding a_1 orbital. The orbital ϕ_3 is antibonding, but the overlap population $n(3, 3\,\mathrm{H}, \mathrm{O})$ decreases to zero by symmetry as the H–O–H angle increases to 120°. The relatively weak bonding of the orbital ϕ_2 may be explained by the fact that the molecule for all the treated angles is rather flat, which diminishes the possibility of the only oxygen $2p$ function of a_1 symmetry, σ_4, joining the $2s$ function to form a strong $2s$–$2p$ hybrid that could make a great contribution to the bond. Therefore, the bonding is predominantly of the weaker $2s$–$1s$ type.

VIII. Electric moment

The center of gravity of the charges is in both the non-flat cases situated somewhat further from the oxygen atom than the center of mass (see Table 6.) This electric moment influences the rotation and vibration spectra of the molecule ion. Any experimental value of the moment has not been found (see discussion).

Table 6. The electric moment of the H_3O^+ ion as a function of the H–O–H angle. In Debye units.

ω	100°	110°	120°
Electric moment	2.96	2.13	0

IX. Discussion

If an experimental value of the electric moment of the H_3O^+ ion could be obtained, it is probable that, in connection with our theoretical study of its dependence on the H–O–H angle, it would give a rather satisfying answer to the question of the real angle. Molecular orbital descriptions usually give passable values of the dipole moments. In addition, the moment in our case varies very rapidly with the angle in the interval 110°–120°, which would make it easier to fix the real value of the angle. In their study of the H_3O^+ ion in crystals of hydrogen halides Ferriso and Hornig [7] found a possible indication of the electric moment. They could not find the band corresponding to the torsional vibrations of the H_3O^+ ions (librations) perpendicular to the symmetry axis. They concluded: "If the bands at 770 cm^{-1} represent this frequency, the dipole moment of the OH_3^+ ion must be very small, at least ten times smaller than in ammonia." If this is true, the moment would be smaller than 0.15 D, which, according to Table 6, would indicate an H–O–H angle only negligibly different from 120°.

This equilibrium angle is also the result of our study of the angular dependence of the total energy. Since, however, the variable part of the total energy is very small compared with the total energy itself, we cannot assign this result any great significance, especially since we have let the O–H distance remain fixed under the angle variation. In ammonia, NH_3, with which H_3O^+ is isoelectronic, the equilibrium H–N–H angle is 107°. In H_3O^+, where the O–H distance is about the same as the N–H distance in NH_3, one can expect the angle to be definitely greater because of the excess charge of the ion, which appears mainly on the hydrogen atoms, thus causing a considerable extra repulsion between them. Concerning the H_3O^+ ion in the experimentally studied crystals, it is probable that the rather different angle values which have been proposed correspond to different values even in reality. The large positive charges of the hydrogen atoms may be a very effective cause for strong bending forces from the frequently ionized neighbouring atoms in the ionic crystals studied. In heavy ice, with a much smaller positive charge on the deutorium atoms, the D–O–D angle is within a half degree of the tetrahedral angle and thus seems to be entirely subordinate to the surrounding crystal structure, which has tetrahedral angles [31, 32]. It is possible that in a future paper we shall be able to obtain more detailed results of the interaction of the hydronium ion with its lattice neighbours. We are especially interested in the properties of the hydrogen bonds where hydronium ions take part. Besides the appearance in ionic crystals like those mentioned earlier, the ion is thought to appear momentarily in hydrogen-bonded systems such as ice, where they are intermediate states in the proton transport process, which is thought to consist partly of proton jumps from one position in a hydrogen bond to the other [2, 3, 33]

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APPENDIX

Three-center integrals

The coulomb interaction one-electron integral $(H_1 : h_2 h_3)$ and the two-electron integrals $(h_1 h_1 : h_2 h_3)$ and $(h_1 h_2 : h_1 h_3)$ have been computed in the following way.

$(H_1 : h_2 h_3)$

This integral has been obtained with four-decimal accuracy by an expansion given by Coulson [21]. It has then been used as the basis for the estimation of other integrals. We have also used other methods in order to compare them and to test their reliabilities in giving values for other integrals; theMulliken approximation [22], where the charge distribution $\psi_1 \psi_2$ is replaced by $\frac{1}{2} S_{\psi_1 \psi_2} (\psi_1 \psi_1 + \psi_2 \psi_2)$, in this case will clearly give a value of the integral which is too low, because it concentrates charge around the two nuclei H_2 and H_3 instead of having constant density on the line H_2–H_3, which is the case here. Along this line the density has its maximum and will decrease rather rapidly beyond it. A $1s_a\, 1s_b$ distribution, where a and b are similiar nuclei therefore may be fairly well represented by a homogeneously charged rod $a\,b$ with total charge $S_{1s_a\,1s_b}$. This approximation gives in our case a somewhat low value (Table 7). The integral has also been approximated with a function of the angle $\phi = \wedge H_2H_1H_3$ in such a way that $S_{h_2h_3}$ comes in as a linear factor:

$$I(\phi) = a\,S(\phi) + b. \tag{7}$$

For $\phi = 0$ the integral reduces to a two-center one and for $\phi = \pi$ it can be calculated exactly according to Barker and Eyring [35]. Then a and b are fixed.

Table 7. The integral $(H_1 : h_2h_3)$ in different approximations. $\omega = 110°$.

Method	$(H_1 : h_2h_3)$
Exact	0.1299
Mulliken approximation	0.1185
$I = a\,S + b$	0.1245
Rod approximation	0.1254

$(h_1h_1 : h_2h_3)$

The Mulliken approximation has been assumed to give the same percentage error in this integral as in $(H_1 : h_2h_3)$.

$(h_1h_2 : h_1h_3)$

The Mulliken approximation of one of the distributions gives two- and three-center integrals of types earlier treated. The same approximation of both the distributions gives only two-center integrals. The results of the two methods for $\omega = 110°$ are 0.0516 and 0.0503 respectively. Here it is more difficult to see if the approximate values, which agree fairly well with each other, lie below or above the correct value. The value 0.0516 is probably the most reliable of them.

Four-center integrals

$(h_1o : h_2h_3)$

The Mulliken approximation of h_1o, which places equal charge on H_1 and O, cannot be suitable for this very unsymmetrical distribution. The refinement of it, the Löwdin approximation [23], consisting in putting $\psi_1\psi_2 = \lambda_1\psi_1\psi_1 + \lambda_2\psi_2\psi_2$, where λ_1 and λ_2 are determined to give the correct total charge and charge moment, is more suitable here. The result is in good agreement with that obtained by the semi point-charge approximation (SPCA) where the h_1o distribution is approximated by a point charge of magnitude S_{h_1o} at the O nucleus (see Table 8).

Table 8. Approximate values of the integral $(h_1o : h_2h_3)$. $\omega = 110°$.

Method	$(h_1o : h_2h_3)$
Mulliken approximation	0.0111
Löwdin approximation	0.0127
SPCA	0.0129

$(h_1 s : h_2 h_3)$

The Mulliken approximation is supposed to give values of this and the integrals earlier studied $(h_1 o : h_2 h_3)$ and $(h_1 h_1 : h_2 h_3)$, which deviate from the exact ones by a factor which depends linearly upon the distance from the centers of gravity of the two charge distributions in question. This corrected Mulliken approximation gives the result 0.0841 for $\omega = 110^\circ$. The Löwdin approximation of $h_1 s$ may be supposed to give a value which is too high because in it charge is moved from the region between the O and H_1 nuclei to the O nucleus, which effect predominates over the contrary effect caused by the corresponding movement of charge to the H_1 nucleus (see Table 9).

Table 9. Approximate values of the integral $(h_1 s : h_2 h_3)$. $\omega = 110^\circ$.

Method	$(h_1 s : h_2 h_3)$
Mulliken approximation of $h_2 h_3$	0.0737
Mulliken approximation of $h_1 s$	0.0809
Corrected Mulliken approximation	0.0841
Löwdin approximation	0.0884

$(h_1 z : h_2 h_3)$

The approximation function

$$I(\varphi) = b \sin \varphi \, S(\varphi), \tag{8}$$

where φ is defined by Fig. 1 and $S(\varphi) = S_{h_2 h_3}$, has the correct value at $\varphi = 0$ and correct derivative $(=0)$ at $\varphi = \pi/2$. We can choose $b = I(\pi/2)$ to give I the correct value at $\varphi = \pi/2$. Its derivative at $\varphi = 0$ is not zero, which would be the case with a function of the type earlier used in (7).

For $\varphi = 110^\circ$ the value obtained is -0.0300, in very good agreement with the value -0.0302 obtained by the Mulliken approximation and corrected with the same factor as for $(h_1 s : h_2 h_3)$ (see Table 10).

Table 10. Approximate values of the integral $(h_1 z : h_2 h_3)$. $\omega = 110^\circ$.

Method	$(h_1 z : h_2 h_3)$
Mulliken approximation	-0.0265
Corrected Mulliken approximation	-0.0302
$b \sin \varphi \, S_{h_2 h_3}$	-0.0300

$(h_1 x : h_2 h_3)$

The Mulliken approximation with the same correcting factor as for $(h_1 s : h_2 h_3)$ and $(h_1 z : h_2 h_3)$ has been used.

Values of the above-mentioned integrals used in our calculations for the different ω values are collected in Table 11.

Table 11. Values of some three- and four-center integrals. (ω defined in Fig. 1.)

Integral \ ω	100°	110°	120°
$(H_1 : h_2 h_3)$	0.1535	0.1299	0.1121
$(h_1 h_1 : h_2 h_3)$	0.1472	0.1257	0.1092
$(h_1 h_2 : h_1 h_3)$	0.0663	0.0516	0.0411
$(h_1 o : h_2 h_3)$	0.0141	0.0129	0.0119
$(h_1 s : h_2 h_3)$	0.0948	0.0841	0.0752
$(h_1 z : h_2 h_3)$	−0.0480	−0.0300	0
$(h_1 x : h_2 h_3)$	0.0254	0.0258	0.0264

Division of Mathematical Physics, Royal Institute of Technology, Stockholm, Sweden.

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